of the geminal anisochronism must be known for each compound in a series. If one has crude qualitative information about chemical shift trends, either from approximate chemical shift theories or from suitable model compounds, this problem will hardly cause difficulties for the large time-averaged chemical shift differences in the series. It becomes progressively more difficult as the numbers approach zero, but, fortunately, this increase in uncertainty is compensated by the corresponding decrease in the importance of sign information for the least-squares calculation. (2) As apparent from the peculiar invariance properties of the model and from Figure 2, applications of the theory require knowledge about the relative ordering of the free energy levels. Here again, crude qualitative information is adequate. Some information of this kind is, in fact, already contained in the ligand constants. For instance, the perhaps somewhat surprising conclusion[4] that phenyl is "smaller" than chlorine only emerged after extensive low-temperature work,[4] but is at once clear from the relative magnitudes of the λ values. (3) We have seen that the model does not yield the absolute populations, since the free energy differences can only be calculated to within a proportionality factor. To extract this factor from time-averaged measurements, one needs values of ⟨Δ⟩ at three, and preferably more, different temperatures.

It is impossible to say at this stage how well the first-order model will perform for other systems. The data are still too limited to exclude the possibility that some of the agreements found in the present paper are accidental. We are inclined to believe, however, that the results are encouraging enough to warrant further efforts.

Acknowledgments. I am indebted to Professor Ivar Ugi, who in a personal conversation in June 1967 implanted the seed of an idea in my mind. Acknowledgment is made to the donors of the Petroleum Research Fund (Grant No. 4440-AC4), administered by the American Chemical Society, for support of this research.

Stable Carbocations. CXLI.[1] The 3-Homoadamantyl Cation

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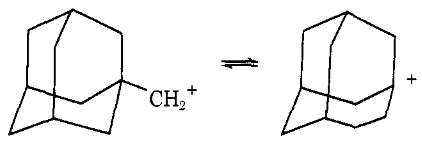
Contribution from the Department of Chemistry, Case Western Reserve University, Cleveland, Ohio 44106. *Received June 17, 1972*

Abstract: The 3-homoadamantyl cation (**1**) was obtained in superacid solutions at −78°. Ion **1** was found to be stable and did not rearrange. Both ^1H and ^{13}C nmr spectroscopic studies indicate the classical nature of the 3-homoadamantyl cation, a trivalent bridgehead carbenium ion. The cage effect in ion **1** was found unimportant in comparison with the 1-adamantyl cation.

The formation of bridgehead carbenium ions,[2] such as the 3-homoadamantyl cation (**1**),[3] has been suggested in connection with studies in the Koch reaction.[3f,4] Solvolysis studies indicated the equilibration between the tertiary homoadamantyl (**1**) and the primary 1-adamantylcarbinyl cation (**2**). However, bridged structure **3** (R = D) of the 3-homoadamantyl cation recently has been suggested as the transition state (or intermediate) involved in the acetolysis of chiral 1-adamantylcarbinyl-*1'-d* tosylate.[5] Schleyer also suggested that simple primary carbenium ions were energetically inaccessible in usual solvolytic systems.[2,5] Theoretical calculation of the stabilities of bridgehead carbenium ions[6] showed that 3-homoadamantyl cation



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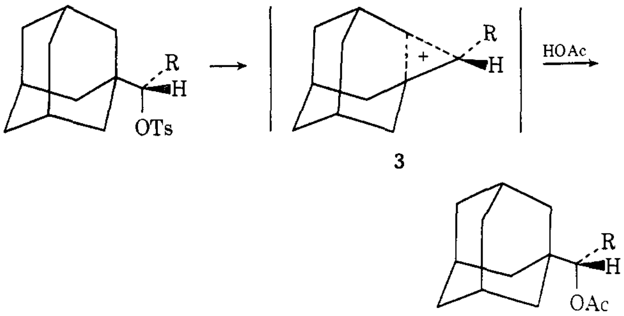

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(1) Part CXL: G. A. Olah, G. D. Mateescu, and Y. K. Mo, *J. Amer. Chem. Soc.*, **95**, in press.

(2) (a) R. C. Fort, Jr., and P. v. R. Schleyer, *Chem. Rev.*, **64**, 277 (1964); (b) U. Schollkopf, *Angew. Chem.*, **72**, 147 (1966); (c) R. C. Fort, Jr., in "Carbonium Ions," G. A. Olah and P. v. R. Schleyer, Ed., Vol. 4, Wiley-Interscience, New York, N. Y., 1972, Chapter 32.

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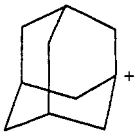
was a substantially stable species, in agreement with the relative solvolytic rates of its derivatives.[3]

In the course of our previously reported work, we have found that tertiary bridgehead carbenium ions, such as 1-adamantyl cation (**4**),[7] 1-bicyclo[3.2.2]nonyl cation (**5**),[8] 9-decalyl cation (**6**),[9] 8-hydrindanyl cation (**7**),[8] and 1-bicyclo[3.3.0]octyl cation (**8**),[10] are sufficiently stable under stable ion conditions to be prepared and studied. We now wish to report the direct observation of the classical tertiary bridgehead 3-homoadamantyl cation (**1**) and its characterization by proton and carbon-13 nuclear magnetic resonance spectroscopy.



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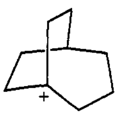

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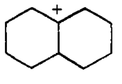

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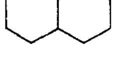

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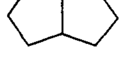

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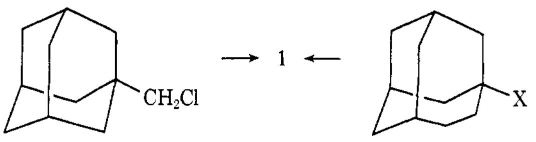
Results and Discussion

3-Homoadamantyl cation (**1**) was prepared from its precursors, 1-adamantylcarbinyl chloride (**9**), 3-homoadamantanol (**10**, X = OH), 3-bromoadamantane (**10**, X = Br), and homoadamantane (**10**, X = H), in FSO_3H–SbF_5–SO_2ClF (SO_2) or SbF_5–SO_2ClF $(SO)_2$ solution at −78°. In all cases ion **1** was stable and cleanly formed in the colorless or slightly yellow solutions. Quenching solutions of the ion with a slurry of a buffered ice in SO_2ClF (SO_2) solution at −78° gave alcohol **10**-OH as the sole identifiable product (by nmr). Ion **1** was found to be stable even when kept at 0° for 2 weeks.



9

10

X = OH, Br or H

The 60-MHz pmr spectrum (Figure 1) of the 3-homoadamantyl cation (**1**) consists of two complicated multiplets centered at δ 2.00 (8 H) and 3.90 (8 H), and a broad singlet at δ 2.70 ppm (1 H). As the pmr spectrum of ion **1** is much more complicated than that of the 1-adamantyl cation (**4**),[7] a complete assignment is difficult. Models show that the adamantyl cage is very much distorted when an additional methylene group is introduced into one of the rings. One of the bridgehead carbon atoms (C_6) is located away from the positively charge center. As the "cage effect" is known in the 1-adamantyl cation,[7] the C_6 bridgehead proton in ion **1** is expected to have a more shielded pmr shift than the other two bridgehead protons, and is assigned to the shift of δ 2.70. The six methylene protons α to the positive charge and the C_1 and C_8 bridgehead protons are assigned to the lowest field peak. Owing to the lack of proper models, the analysis of the pmr spectrum is incomplete but suffices for evaluating the major structural properties.[11]

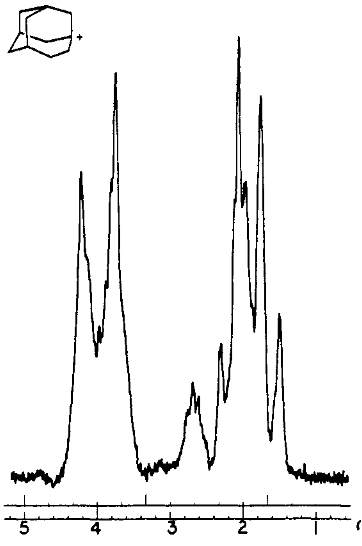
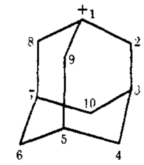


Figure 1. The 60-MHz pmr spectrum of the 3-homoadamantyl cation at −60°.

Since ^{13}C nuclear magnetic resonance spectroscopy is a more sensitive tool for revealing electronic structure,[12] we have obtained the ^{13}C chemical shifts of ion **1** using the fast Fourier-transform method.[13] A comparison of ^{13}C chemical shifts of the 3-homoadamantyl cation and the 1-adamantyl cation is shown in Table I.

Table I. ^{13}C Nmr Parameters of Adamantyl (**4**) and Homoadamantyl (**1**) Cations



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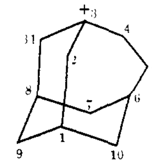

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4		1	
Carbon	$\delta_{^{13}C}$	Carbon	$\delta_{^{13}C}$
C_1	−106.0	C_3	−110.9
C_2,C_8,C_9	+128.0	C_2,C_{11}	+128.1
C_3,C_5,C_7	+107.0	C_4	+143.2
C_4,C_6,C_{10}	+160.0	C_5	+156.4 (or +175.9)
		C_6	+164.2
		C_1,C_8	+136.4
		C_7,C_{10}	+159.0
		C_9	+175.9 (or +156.4)

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(8) G. A. Olah, G. Liang, J. R. Wiseman, and J. A. Chong, *ibid.*, **94**, 4927 (1972).

(9) G. A. Olah, D. P. Kelly, and R. G. Johanson, *ibid.*, **92**, 4137 (1970).

(10) (a) G. A. Olah and G. Liang, *ibid.*, **93**, 6873 (1971); (b) G. A. Olah, J. M. Bollinger, and D. P. Kelly, *ibid.*, **92**, 1432 (1970).

(11) The 100 MHz pmr spectrum of 3-homoadamantyl cation, obtained by using a Varian HA100 spectrometer, also shows insufficient resolution of all the signals. It is not expected that a 220 MHz pmr spectrum would much improve resolution.

(12) (a) G. A. Olah and A. M. White, *J. Amer. Chem. Soc.*, **91**, 5801 (1969), and references quoted therein; (b) J. B. Stothers, *Quart. Rev., Chem. Soc.*, 144 (1965).

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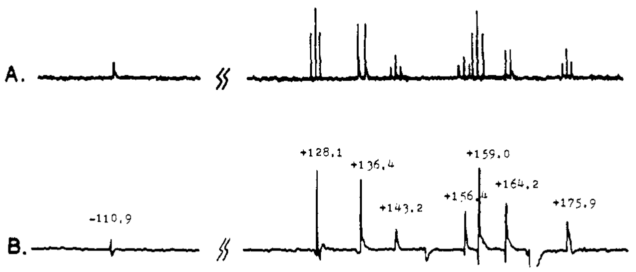


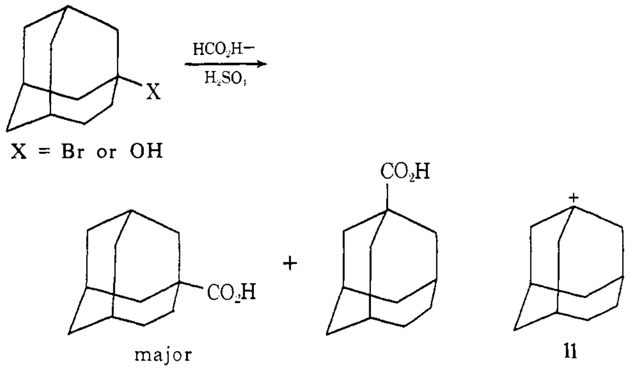
Figure 2. The carbon-13 nmr spectrum of the 3-homoadamantyl cation in FSO_3H–SbF_5–SO_2ClF at −60°: (A) off-resonance spectrum; (B) completely decoupled spectrum.

The completely decoupled ^{13}C nmr spectrum[13] (Figure 2B) of the 3-homoadamantyl cation shows eight single lines at $\delta_{^{13}\text{C}}$ −110.9 (1 C), +128.1 (2 C), +136.4 (2 C), +143.2 (1 C), +156.4 (1 C), +159.0 (2 C), +164.2 (1 C), and +175.9 (1 C). The most deshielded carbon chemical shift, −110.9, is naturally assigned to that of the carbenium bridgehead carbon (C_3). This shift is only about 5 ppm more deshielded than that of the corresponding bridgehead carbenium carbon (C_1) in the 1-adamantyl cation. The small difference might be due to the more planar bridgehead sp^2 conformation in ion **1**. The other three equivalent bridgehead carbons (C_3, C_5, and C_7) of ion **4** have shifts $\delta_{^{13}\text{C}}$ +106.0 whereas those of ion **1** are different, and their shifts are considerably shielded. The assignment of the bridgehead carbon chemical shifts was made from the cmr spectrum with the off-resonance decoupling technique[13] (Figure 2A) in which all the methylene carbon signals become triplets, while all the bridgehead carbon signals become doublets, as two protons and one proton, respectively, are attached to them. Thus the three bridgehead carbons C_1, C_8, and C_6 are assigned to have the chemical shifts $\delta_{^{13}\text{C}}$ +136.4, +136.4, and +164.2, respectively. One would expect that the flattening of the bridgehead carbenium center and the introduction of the extra methylene group into the cyclohexyl ring would considerably weaken the overlap between the empty p orbital and the backside of the three sp^3 bridgehead C–H orbitals. Also, the back lobe of the empty p orbital of the bridgehead carbenium center cannot symmetrically extend into the homoadamantane cage. The highly shielded bridgehead carbon chemical shifts in ion **1** might be an indication that the cage effect here is not as important as in 1-adamantyl cation. Although ion **4** has a uniquely favorable geometry for achieving this effect through backside orbital charge delocalization,[2a,3d,7] its existence has recently been seriously questioned on the basis whether such an effect is actually operative and, even if so, whether it is of sufficient magnitude to account for the observed data.[6a] We feel that in comparison with data of ion **4** the deshielded bridgehead proton and carbon chemical shifts of ion **1** are indeed revealing the importance of the cage effect in the 1-adamantyl cation **4**.

The observation of eight lines in the cmr spectrum (Figure 2B) of ion **1** are indicative of the plane of symmetry of the ion. Thus the carbon chemical shifts of C_2 and C_{11}, C_1 and C_8, and C_7 and C_{10} should be identical, and are assigned $\delta_{^{13}\text{C}}$ +128.1 ppm, +136.4, and +159.0, respectively. The carbon (C_4) β to the positive charge is assigned to shift $\delta_{^{13}\text{C}}$ +143.2, which is 15.2 ppm more shielded than that of the corresponding carbon in ion **4**. The other two methylene carbons, C_5 and C_9, are assigned the shifts at $\delta_{^{13}\text{C}}$ +156.4 and +175.9, respectively. According to the model, ion **4**, C_9 in ion **1** should have similar carbon shift as that of C_6 in ion **4** ($\delta_{^{13}\text{C}}$ +160). The shift of +156.4 then should be assigned to C_9. However, C_5 in ion **1** is at a γ position to the positive charge. It might have a more deshielded carbon shift than C_9. In this case, the 1-adamantyl cation does not seem to be a suitable model for ion **1**. Differentiation between C_5 and C_9 therefore cannot be made with certainty at this point.

Although the acetolysis of homoadamantyl derivatives[2,3] yields both 3-homoadamantyl and 1-adamantylcarbinyl products, the tertiary 3-homoadamantyl cation (**1**) is apparently the most stable species under the stable ion conditions studied in this work. Considering the nonclassical bridged structure **3**, suggested as the transition state in the conversion of derivatives of ion **2** into that of ion **1**, we feel that there is little possibility for such an ion to make a significant contribution to the structure of the stable intermediate in superacid solutions. Further, a carbon shift of −110.2 ppm for the bridgehead carbenium center argues against any substantial buildup of positive charge at C_4 in ion **1**. This does not imply however that under solvolytic conditions bridged structure **3** cannot contribute.

Koch reactions of homoadamantyl systems have recently been reported to yield a mixture of 1- and 3-homoadamantanecarboxylic acids.[4a] One thus might expect the possibility for the 1-homoadamantyl cation (**11**) to also exist in superacid solutions. However, ion



11, if it exist, should be more symmetrical and to have only seven different kinds of carbons. The cmr spectrum of ion **1**, however, shows eight different carbons, which is consistent with the 3-homoadamantyl cation formulation. Schleyer and his coworkers[6b,c] have recently calculated the relative strain energies of the 1- and 3-homoadamantyl cations. The 3-homoadamantyl cation (**1**) is indicated to be substantially more stable and this is supported by the relative solvolysis rates of the 1- and 3-homoadamantyl bromides.[2] Further evidence is given by the fact that only ion **1**, not **11**, is formed when homoadamantane (**10**, X = H) is treated with SbF_5 or FSO_3H–SbF_5 in SO_2ClF solution at −78° (hydrogen abstraction), although there is equal opportunity for either one of the two bridgehead hydrogen atoms (C_1 or C_3) to be ionized. The fact that only C_3–H is ionized shows that the 3-homoadamantyl cation (**1**) is indeed more stable than the 1-homoadamantyl cation (**11**). Further, the cmr spectrum of ion **1** clearly consists of eight lines. The presence of even low concentrations of 1-homoadamantyl cation should immediately complicate the Fourier-transform cmr spectrum of ion **1**. This was not found to be the case.

One might also have expected that some methyladamantyl derivatives would also be found in the system. Yet we do not find evidence for the presence of any methyladamantyl derivatives in the quenching experiments.

Taken altogether, the evidence presented clearly indicates the classical, carbenium ion nature of the 3-homoadamantyl cation, and that a cage effect is not important in this case. Determination of the exact geometry of the cation will necessitate further experimental work (including X-ray study). "Cage effects" have been suggested as important factors responsible for the deshielding effect of bridgehead carbon and proton nmr shifts in 1-adamantyl[7] and 1-bicyclo[3.2.2]nonyl[8] cations. The insignificance of such an effect in the distorted 3-homoadamantyl cation (**1**) seems to indicate that suitable geometry is the primary requirement for such effects.

Experimental Section

1-Adamantylcarbinyl chloride (9) and **3-homoadamantanol (10)** were prepared according to literature procedures.[3b,c]

Quenching of solutions of 3-homoadamantyl cation were carried out in KOH–ice/SO_2ClF by the previously described procedure.[14]

Preparation of the 3-Homoadamantyl Cation (1). $FSO_3H–SbF_5$ (1:1) or a saturated solution of SbF_5 in SO_2ClF (SO_2) was prepared and cooled to Dry Ice–acetone bath temperature, *ca.* −78°. To the solution was then slowly added with vigorous stirring a cold solution of **9** or **10** in SO_2ClF (SO_2) to give an approximately 15–20% solution of the ion, which was then transfered to a precooled nmr tube.

Nuclear Magnetic Resonance Spectra. Proton nuclear magnetic resonance spectra (60 MHz and 100 MHz) were obtained by using a Varian Associates Model A56/60A and HA100 nmr spectrometer, respectively. External TMS (capillary tube) was used as reference. Carbon-13 nuclear magnetic resonance spectra were obtained by the fast Fourier-transform method, using Varian HA-100 nmr spectrometer equipped with a variable-temperature probe. Either external methyl iodide or carbon disulfide was used as reference. Carbon chemical shifts were obtained with respect to the external methyl iodide as reference and converted to the carbon disulfide standard. A value of 208.7 ppm was used for $\delta_{^{13}CH_3I}$ (SO_2ClF, −60°). Off-resonance decoupled cmr spectra[13] were obtained with a coherent radiofrequency, using external CS_2 as reference.

Acknowledgment. Support of our work by the National Science Foundation and Petroleum Research Fund administered by the American Chemical Society is gratefully acknowledged, as are stimulating discussions with Professors Paul v. R. Schleyer and J. Eric Nordlander.

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Reaction of Selenium with Sodium Borohydride in Protic Solvents. A Facile Method for the Introduction of Selenium into Organic Molecules

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Abstract: Elemental powdered selenium and sodium borohydride react very readily in water or ethanol to give either sodium hydrogen selenide or sodium diselenide, depending on the ratio of the reactants. The sodium hydrogen selenide and sodium diselenide solutions, thus prepared, can be utilized directly in typical nucleophilic displacement reactions.

Alkali metal borohydrides have been combined with the chalcogen elements by direct fusion[1,2] and in aprotic solvents such as ether,[2] dioxane,[3] tetrahydrofuran,[4,5] and diglyme.[4,5] Under the latter conditions, sulfur, selenium, and tellurium were incorporated directly into the borohydride.[4,5] The product of the reaction between selenium and sodium borohydride was reportedly difficult to isolate and its structure was suggested to be $NaBH_2Se_3$.[5]

We have found that, in protic solvents such as water or ethanol, powdered gray selenium reacts rapidly and exothermically at room temperature with sodium borohydride to produce sodium hydrogen selenide (NaHSe) or sodium diselenide (Na_2Se_2), depending on the borohydride to selenium ratio.

Results and Discussion

Sodium Hydrogen Selenide. With a 2:1 molar ratio of borohydride to selenium in water, the reaction proceeded according to eq 1 with hydrogen evolution and

$$4NaBH_4 + 2Se + 7H_2O \longrightarrow 2NaHSe + Na_2B_4O_7 + 14H_2 \quad (1)$$

the formation of sodium hydrogen selenide and sodium

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